ELECTRON EMISSION CURRENTS OF METALS
COVERED WITH ATOMIC LAYERS

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16. Abstract   A physical model is given for the evaporation equilibrium process of atoms on electron emitters made of metal; concrete parameters may be placed into a general framework. The model considered here explains the experimental results in a qualitatively correct manner. For the quantitative interpretation of the measured curves, additional assumptions and sophistications are needed. By means of an experimental example the great importance of an adequate calculation of the average work function and emission current density is demonstrated.

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ELECTRON EMISSION CURRENTS OF METALS COVERED WITH ATOMIC LAYERS

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Introduction

In electron emitters, covering with atomic layers plays an important role, since impurities in the environment are almost universal. Even with a good vacuum (10^{-8} torr), it takes only a few seconds for a previously clean, cold surface to become covered. Langmuir [6], Rasor [7], et al. have reported semi-empirical relations giving the emission current as a function of temperature for specific combinations of materials. The following article will show the general evaporation equilibrium process of atoms, and not inherent, substance-specific temperature dependences; the point at which substance-specific details enter will also be indicated. The object of this study is not to compute the physical parameters (e.g. the work function) for specific combinations of substances[1], but to give a general framework into which such concrete parameters can be placed. The great importance of correct averaging in the calculation of the function for covered surfaces will be indicated. Using an experimental current density/temperature curves, we will show how large the differences produced by various averaging methods can be. This problem is also important for thermionic converters.

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[1] After handing in the present work to the printers (Sept. 1965), studies were published concerning this subject, such as those listed in the references under [9] and [10].

* Numbers in the margin indicate pagination in the foreign text.

1. Principles

In order to make the geometrical relationships as simple as possible, a plane arrangement is taken as a base, in which electron emitter and evaporator stand opposite each other. While the evaporator has a homogeneous surface, the emitter is covered with the evaporator substance, to a degree of covering Θ (Fig. 1).
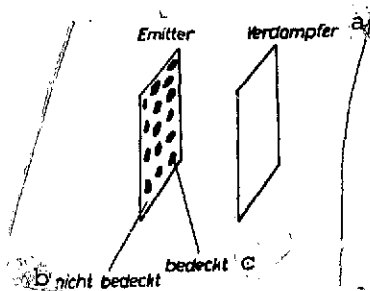

Fig. 1. Diagrammatic sketch of emitter and evaporator arrangement.

Key: a. Evaporator; b. Uncovered; c. Covered

Let the spots on the emitters be at first any size desired; they may even be within atomic dimensions. In the following, it will be assumed, as usually applies, that under the present conditions monatomic layers adhere more firmly to the base metal of the emitter than to the basic material of the evaporator, so that the adsorption enery E_A is greater on the emitter than on the evaporator. The result is that the emitter is relatively well covered even for temperatures considerably above the evaporator temperature. Moreover, primarily those atoms are adsorbed and adhere longer to the emitter that meet the still-uncovered areas. The problem then is to determine the equilibrium condition for evaporation, both on the electron emitter and on the evaporator, for various temperatures. One first obtains the degree of coverage as a function of temperature. It is thus easy to compute the course of the emission current. In the following derivations, some simplifications will be used, which, however, do not affect essentials, so that their subsequent elimination is possible if necessary. In general, however, the results of these approximation relationships should adequately report the course of the emission current.

Let the number of atoms being evaporated per unit time and area be called G. This particle current density depends exponentially on the bond energy and temperature:

$$G = K \cdot \exp[- E_A/kT]$$ (1)

In detailed studies, K is shown to be not always entirely independent of temperature; however, this is unimportant in this case, since the exponential function remains dominant.

The atoms evaporated from the evaporator and electron emitter either go directly to the opposite electrode or form an intervening gas with pressure p, if the free path length is smaller than the distance between electrodes. These two limit cases will be considered separately in the following study, although the results show only insignificant differences.

2. Computation of Degree of Coverage Θ

2.1. Free Path Length << Distance between Electrodes

The pressure p of the gas between the electrodes is independent of location. Because of the difference in electrode temperature, the gas density then differs in front of the emitter from the front of the evaporator:

$$p_V = n_V \, kT_V = p_E = n_E \, kT_E$$ (2)

$$n_V/n_E = T_E/T_V$$ (3)

On the emitter a diffusion current flows onto the surface in the quantity

$$G_{E\ominus n} = \frac{n_E \bar{v}_E}{4}$$ (4)

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of which, however, according to the hypothesis, in practice only that part remains adhering which meets the uncovered portions:

$$G'_{E\,on} = \frac{n_E \bar{v}_E}{4}(1-\theta)$$ (5)

At the same time, atoms are evaporated from the covered places:

$$G_{E\,off} = K_E \cdot \exp\left[-\frac{E_{AE}}{kT_E}\cdot\right]\cdot\theta$$ (6)

The equilibrium condition must be

$$G_{E\,off} = G'_{E\,on}$$ (7)

Similar relations apply on the evaporator; of course, here the degree of coverage is to be placed equal to zero:

$$G_{v\,on} = \frac{n_v \bar{v}_v}{4} = K_v \cdot \exp\left[-\frac{E_{AV}}{kT_v}\right] = G_{v\,off}$$ (8)

Equations (7) and (8), of course, only apply for a complete equilibrium, i.e., when the degree of coverage on the emitter remains constant over time as long as the temperatures do not change. In an equilibrium, the quantity of gas between electrodes also remains constant, if peripheral losses are ignored. If the measurement apparatus selected does not permit such losses to be disregarded, then G_v off in equation (8) must be increased with regard to G_v on by an amount so that the losses are covered and equation (7) again applies. From equations (5)-(8) results, with the aid of equation (3)

$$(1-\theta)\frac{T_v \bar{v}_E}{T_E \bar{v}_v}K_v \cdot \exp\left[-\frac{E_{AV}}{kT_v}\right] = \theta \cdot K_E \cdot \exp\left[-\frac{E_{AE}}{kT_E}\right]$$ (9)

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This may be simplified if one considers the relationship

$$\bar{v}_E / \bar{v}_V = \sqrt{T_E / T_V} \tag{10}$$

so that

$$\sqrt{T_V / T_E} \cdot K_2 \cdot \exp\left[-\frac{E_{AV}}{kT_V}\right] = \frac{\theta}{1-\theta} K_1 \exp\left[-\frac{E_{AE}}{kT_E}\right] \tag{11}$$

The desired dependence of the degree of coverage on the temperatures of the emitter and the evaporator is obtained from equation (11) by solving for θ:

$$\theta = \left(1 + \frac{K_E}{K_V}\sqrt{\frac{T_E}{T_V}}\exp\left[\frac{E_{AV}}{kT_V} - \frac{E_{AE}}{kT_E}\right]\right)^{-1} \tag{12}$$

According to equation (12), the degree of coverage, as the experiment also requires, is 1 for low emitter temperatures and falls steeply toward zero as soon as the current density of evaporated particles at the emitter exceeds that at the evaporator (Fig. 2). The square root obtained from the temperature correla-

Fig. 2. Diagrammatic dependence of degree of coverage on emitter temperature.

tion which appears as a factor in equation (12) plays only a subordinate role. Of course, in practice multiple layers occur for low temperatures. This is not described by equation (12), since, according to definition, θ may not be greater than 1.
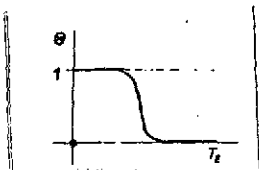
2.2. Free Path Length >> Distance between Electrodes

In this case, no actual gas exists; each evaporated particle goes to the opposite electrode. Part of the substance from the evaporator will even go to covered portions

and form multiple layers, although, according to the hypothesis, these are more easily evaporated again. Consequently, a degree of multiple coverage Θ_1, indicating the portion of surface with multiple layers, will be introduced in the following in addition to the degree of coverage Θ, giving the portion of area which is covered at all. The atoms which are deposited over the monatomic base layer are, as a first approximation, bound to their base layer as to the evaporator. The same parameters are therefore in effect. In the temperature range of interest, i.e., for T_E which are not too low, one may definitely place $\Theta_1 \ll \Theta$. Thus, for evaporation on the emitter there applies
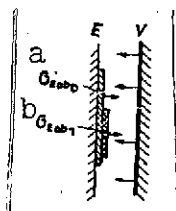
Fig. 3. Evaporator and emitter with partial multiple covering for $\lambda \gg d$.
Key:
a. $G_{E off_0}$
b. $G_{E off_1}$

$$G_{E off} = \Theta K_E \exp\left[-\frac{E_{AE}}{kT_E}\right] + \Theta_1 \cdot K_V \cdot \exp\left[-\frac{E_{AV}}{kT_E}\right] \tag{13}$$

and in addition in an equilibrium

$$G_{E off} = G_{V on} = K_V \cdot \exp\left[-\frac{E_{AV}}{kT_V}\right] \tag{14}$$

Opposite the covered portion Θ of the emitter surface there stands an evaporator area of the same size. In this connection it is supposed that all atoms move perpendicularly to the surfaces. Since in equilibrium Θ_1 must also be constant, the particle current which meets the covered portion Θ of the opposite, equal evaporator surface is equal to the particle current which evaporates from the multiple layers:

$$\Theta K_V \exp\left[-\frac{E_{AV}}{kT_V}\right] = \Theta_1 K_V \exp\left[-\frac{E_{AV}}{kT_E}\right] \tag{15}$$

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With equation (15), Θ_1 can be eliminated from equation (13), and, together with equation (14), there results

$$\Theta \cdot K_E \cdot \exp\left[-\frac{E_{AE}}{kT_E}\right] + \Theta \cdot K_v \cdot \exp\left[-\frac{E_{AV}}{kT_V}\right] = K_v \cdot \exp\left[-\frac{E_{AV}}{kT_V}\right]$$

(16)

or

$$\Theta = \left(1 + \frac{K_E}{K_v}\exp\left[\frac{E_{AV}}{kT_V} - \frac{E_{AE}}{kT_E}\right]\right)^{-1}$$

(17)

Up to the factor $\sqrt{T_E/T_V}$, this expression agrees with equation (12). If one increases the electrode interval from very small values to considerably above the free path length, the degree of coverage corresponding to this factor becomes somewhat less, because of the gas between the electrodes. However, this factor is not very important, and the curve sketched in Fig. 2 also applies to equation (17).

3. Electron Work Function

It is known that extraneous layers which are adsorbed on the surface form electric dipole layers and thus may considerably alter the effective work function. The strong combining forces on the surface lead to polarization even of molecules which polarize with difficulty. With multiple layers, the uppermost layer is combined approximately in the same way as on the evaporator. Polarization and work function must, consequently, also agree with those of the evaporator. However, according to the hypothesis, a monatomic layer is more firmly bound to the metal. Stronger polarization may be combined with this than occurs on the evaporator substance, so that the work function of the metal with a monatomic covering may be somewhat smaller than that of either the evaporator or the emitter metal, if the vector of

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the dipole moment of the layer is directed away from the emitter. This minimal work function increases with greater covering to that of the evaporator material. Larger areas with monatomic covering thus either have the work function of the evaporator or, in case of the polarization effect mentioned above, have the minimal work function. This depends on the evaporator material. In the following, let it be left open what numerical value is to be inserted for the work function eU_{a2} of the area completely covered with a monatomic layer. In any case, eU_{a2} is at least very near the evaporator work function. The emitter surface consists of uncovered areas with the undisturbed work function $e\,U_{aE}$ and covered areas with $e\,U_{a2} \approx e\,U_{aV}$.

Of particular interest is the case $U_{a2} < U_{aE}$ (e.g., Cs., Ba, or LaB_6 on W). The surface potential of these areas differs, so that electric fields arise on the boundaries between areas (Fig. 4). The areas with smaller work function are positive as
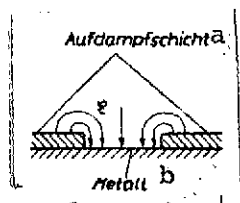
Fig. 4. Boundary field spots for partially covered metal.

Key: a. Deposited layer; b. Metal

compared with their surroundings. The fields are directed in such a way that they hinder electron emission from areas with a small U_a and favor emission from areas with a large U_a; thus they have an equalizing effect. For the first time in the present considerations, the size of the spots begins to play a role. The fields have an effect only in a narrow boundary zone, which is on the order of magnitude of a few layer thicknesses (atom diameters). In spite of the uniform degree of coverage, the deposited material may be finely distributed, consisting in the limiting case of individual, unconnected atoms, or growing together to larger size. In the first case, the average value of the work function also has an effect on electron emission; in the second case, the emission of the two areas is independent of one another, each with its own work function. The average

value of the work function does not then determine the total emission current, but rather would result as a measured value, e.g., in the determination method using a vibrating capacitor. This average value is given by

$$\overline{U}_a = \theta U_{a2} + (1 - \theta) U_{aE} = U_{aE} - \theta (U_{aE} - U_{a2})$$

(18)

One then obtains the curve diagrammed in Fig. 5.

When the polarization effect mentioned above occurs, the broken line applies. That value of U_{a2} is to be inserted which applies for a small θ, up to $\theta = 1$. Thus, with a very pronounced minimum, the minimal value of $\overline{U}_a$ is to be inserted, not the value applying for $T_E \leftarrow 0$. Cases in which the atoms deposited on the emitter become ionized and are evaporated as ions (e.g., Cs on W) must be excluded for the present, since in this case other energy values apply.
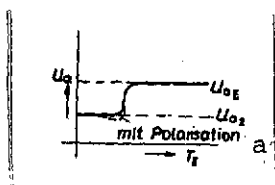

Fig. 5. Dependence of work function on emitter temperature.

Key: a. With polarization

4. Emission Current

With a finely distributed covering, in the Richardson-Duschman formula the average work function can be inserted according to equation (18) and one obtains for the density of the electric saturation current

$$S_{el} = A T_E^2 \exp \left[-\frac{e \overline{U}_a}{k T_E} \right]$$
$$= A T_E^2 \exp \left[-\frac{e}{k T_E} (U_{aE} - \theta (U_{aE} - U_{a2})) \right]$$

(19)

If one plots this current density logarithmically over $1/T_E$, the curve shown in Fig. 6 results. This curve also results

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experimentally. The current curve follows the emission line which is characteristic of the emitter metal for high temperatures ($\Theta = 0$) and passes into the line of the evaporator material with an increasing degree of coverage ($\Theta = 1$).
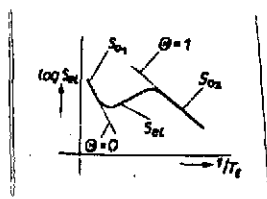

Fig. 6. Diagram of emission current in semilogarithmic presentation.

In the case of covering with large spots and large intervening uncovered areas, the emissions of the two areas are almost independent of one another, since the boundaries of the spots then have no great effect. In correspondence with the surface components, the current is composed as follows:

$$S_{el} = (1 - \Theta) A T_E^2 \exp\left[-\frac{e\,U_{aE}}{kT_E}\right] + \Theta A T_E^2 \left[-\frac{e\,U_{a2}}{kT_E}\right]$$
$$= (1 - \Theta) S_{01} + \Theta S_{02} = S_{01} + \Theta (S_{02} - S_{01}) \qquad (20)$$

S_{01} is the current density of the uncovered metal, S_{02} that of the completely covered metal. From equation (20) results a curve shape resembling that diagrammed in Fig. 6. However, the degree of coverage according to equation (19) passes much more sharply into dependence on temperature than according to equation (20). Reality must lie between the two extremes. There are very many individual molecules, but also some spots where molecules have grown together. With a gradual depositing (no spraying of the evaporator), especially for monocrystal surfaces, the layer form must approach quite closely that assumed as finely distributed in equation (19).

The constant A, which helps to determine the emission current in equations (19) and (20), will henceforth be regarded as a real constant, although it is known that in practice this is not so. In general this variability is traced, at least in part, to the temperature dependence of the work function. For the great change in $\overline{U}_a$ which is treated here, such effects are contained to

begin with the exponents in equation (19). A second effect is also operative, especially for a semiconducting evaporator material (BaO), leading to reductions in the constant A for multiple layers as compared with a monatomic layer on metal. Because of the significantly less carrier content of the poorly conducting semiconductor base, much fewer electrons are brought to the surface for emission than with a metal base.

5. Determination of Bond Energies from Experimental Curves

If equation (20) is valid, the degree of coverage can easily be obtained from experimentally measured current density curves (corresponding to Fig. 6):

$$\theta = \frac{S_{e1}(T_E) - S_{01}(T_E)}{S_{02}(T_E) - S_{01}(T_E)} \Bigg|$$

(21)

For this purpose, the lines for S_{01} and S_{02}, according to Fig. 6, are plotted as tangents to the measured curves; one may then read the values of $S_{e1}(T_E)$, $S_{01}(T_E)$, and $S_{02}(T_E)$ for all T_E, and one may compute θ, by points, according to equation (21). Of course, the shape corresponds to that in Fig. 2, and the average value $\overline{U}_a$ which can be obtained from it corresponds to the curve in Fig. 5. One may also attempt to obtain the adsorption energy E_{AE} and E_{AV} from the measured curves. For this one may use the slope of the curves in the transition area between relative minimum and relative maximum, according to Fig. 6. One first finds the temperature with $\theta = 1/2$. Then $S_{e1}^* = S_{e1}/AT_E^2$ is plotted logarithmically over $1/kT_E$. The slope, $\partial(\log S_{e1}^*)/\partial(1/kT_E)$, then becomes for $\theta = 1/2$:

$$b = \frac{\partial \ln S_{e1}^*}{\partial(1/kT_E)} \Bigg|_{\theta=\frac{1}{2}} = \frac{1}{2} E_{AE} - e U_{a2} \Bigg|$$

(22)

or

$$E_{AE} = 2(b + e U_{a2}) \Bigg|$$

(23)

One may find U_{a2} and U_{aE} from the slope of the logarithmic lines S_{01} and S_{02}. The values thus computed are usually too large, since covering with large spots represents only one extreme case. The other extreme case is given by a covering which is completely uniform and finely distributed atomically; for this equation (19) applies.

The measurements interpreted below were made under conditions closely approaching the hypotheses for equation (19). This equation should therefore be discussed in somewhat more detail. Here again computation is made with the reduced current density $S_e^* = S_{e1}/AT_E^2$. The slope is then obtained:

$$b = \frac{\partial \ln S_{e1}^*}{\partial (1/kT_E)} = -eU_{aE} + \theta e(U_{aE} - U_{a2})$$
$$+ e(U_{aE} - U_{a2})\frac{E_{AE}}{kT_E}\theta(1 - \theta) \qquad (24)$$

To locate the relative minimum in the logarithmic curve, a simple extreme value analysis, with $kT_E/E_{AE} \ll 1$, results in:

$$\theta_{min} \approx \frac{kT_E}{E_{AE}}\left(1 - \frac{kT_E}{E_{AE}}\right)\frac{U_{aE}}{U_{aE} - U_{a2}} \qquad (25)$$

The maximum is found by

$$\theta_{max} \approx 1 - \frac{kT_E}{E_{AE}}\frac{U_{a2}}{U_{aE} - U_{a2}} \qquad (26)$$

It is important to locate the point of inflection of the curve.
With the usual methods of differential calculus, one obtains

$$\theta_w = \frac{1}{2} + \frac{kT_E}{E_{AE}} \qquad (27)$$

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The point of inflection is located near $\Theta = 1/2$. However, if one reads the slope for $\Theta = 1/2$ one obtains from a single conversion of equation (24)

$$E_{AE} = \frac{2b_w + e(U_{aE} + U_{a2})}{e(U_{aE} - U_{a2})} \cdot 2kT_E$$

(28)

Fig. 7 exemplifies two measured current density curves.[2] The measurement apparatus was a diode with a filamentary emitter, which was heated electrically and was surrounded by a small molybdenum tube. The latter could also be heated and had a relatively thick inner layer of BaO. The small tube served as both evaporator and anode. Equation (28) yields a bond energy for the molecule deposited on the tungsten emitter of 2.5 eV; in contrast, equation (23) yields ca. 8.5 eV. A mixture of BaO and Ba is deposited.

The actual value lies between the two extremes. This is understandable if one considers the surface structure of the polycrystalline tungsten. The work function differs for different surfaces of a tungsten crystal, varying between 4.2 and 5.6 eV [2]. The surfaces of the crystal are not covered at the same rate. For example, with a drop in temperature, for average Θ the outside crystal planes, with a large work function, are completely covered when other planes are only beginning to be covered. This causes a surface to be covered with large spots within which there is a very fine distribution. This mixed structure results in a bond energy which is between the boundary values given above.

From data given in the literature [3, 4], the bond energy E_{AV} of BaO on the evaporator can be computed as ca. 4 eV. The bond energy, E_{AE}, on the tungsten emitter would then have to be

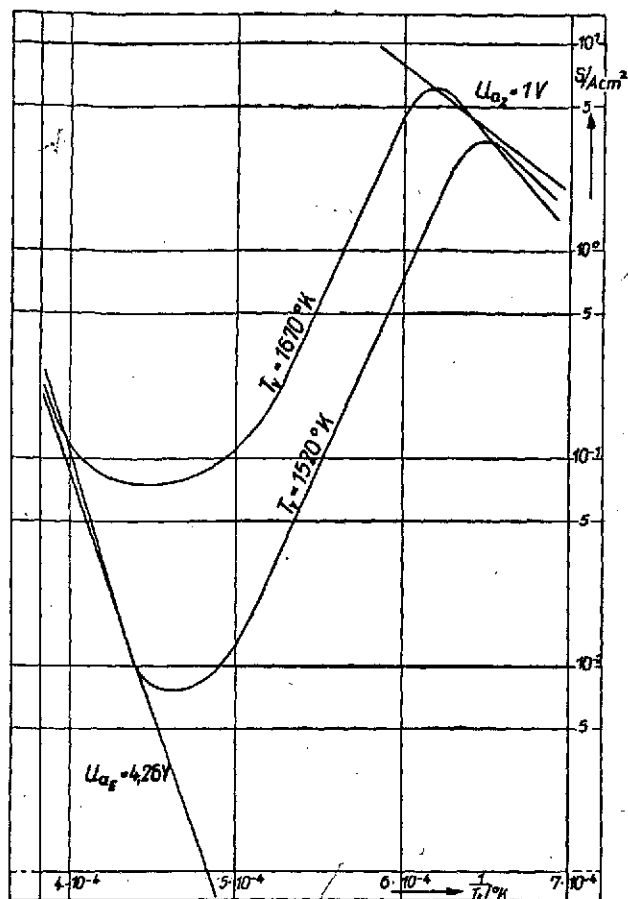[2] The measured curve in Fig. 7 was plotted by Mr. Partsch.

Fig. 7. Measured emission current of a W-emitter with an inner layer of BaO/Ba. Parameter: evaporator temperature.

larger than 4 eV, according to the above hypothesis that bonding is stronger on the emitter than on the evaporator. These relationships are accurate when measurements is begun. However, there ensues on the tungsten emitter the reaction

$$6\,BaO + W = Ba_3\,WO_6 + 3\,Ba$$
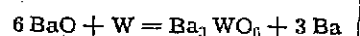
with an activation energy of 3.4 eV [5]. The evaporated barium then returns to the evaporator, so that after a period of adjustment the more volatile barium dominates the evaporation process. Energies of 2.5-3 eV are reported for evaporation of Ba from metal capillary cathodes, with a BaO supply [4]. However, these values cannot be simply accepted as such, since in these cathodes several physical processes must take place in succession (evaporation of BaO supply, chemical liberation of Ba, transport of Ba through porous tungsten substance, etc.). For example, if evaporation is primarily limited by the transport process in the tungsten, then in interpreting the temperature dependence of evaporation one measures the energy of activation of this process. In general, one finds a sum of several processes which together determine the total process. Since geometrical effects are also important (e.g., number and size of pores), even a component process with a

relatively small activation energy may become limiting. The bond energy of Ba to BaO is probably between 2 and 3 eV, that of Ba to W between 3 and 4 eV.

The great differences in the computed values obtained from equations (23) and (28) show the important effect of the physical model selected for the physical data obtained. This role of the physical model is clear in the above interpretations, since purely formal, mathematical formulations, which have often been used for adjustment to specific measurements, were not used. At the same time, points of contact result for sophistication of these theoretical considerations. For example, it was assumed that the bond energy falls suddenly from the value of the first surface layer ($\theta < 1$) to the smaller value of the evaporator when multiple layers are beginning to be formed by further covering. /892 Of course, this transition is smoothed out because of the reciprocal effect of the adsorbed atoms on one another.

In this connection, it would also be interesting to investigate single crystals, for which equation (19) must apply with good approximations.

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